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14. ABSTRACT
In this project we have made strides towards developing a mesoscopic statistical framework (MSF) to model non-equilibrium ensembles comprised of large numbers of simple components. As a testbed, we have considered inhomogeneity formation in driven non-equilibrium systems, namely we seek to predict whether inhomogeneities appear and to develop a description of inhomogeneity formation that is valid across particle and system scales. These systems can be tricky to analyze as mesoscale structures can lead to highly nonlinear macroscopic responses e.g. near a critical concentration, the effective yield stress and viscosity of a suspension may increase by many

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Report Title

Final Report: Developing Novel Frameworks for Many-Body Ensembles

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In this project we have made strides towards developing a mesoscopic statistical framework (MSF) to model non-equilibrium ensembles comprised of large numbers of simple components. As a testbed, we have considered inhomogeneity formation in driven non-equilibrium systems, namely we seek to predict whether inhomogeneities appear and to develop a description of inhomogeneity formation that is valid across particle and system scales. These systems can be tricky to analyze as mesoscale structures can lead to highly nonlinear macroscopic responses e.g. near a critical concentration, the effective yield stress and viscosity of a suspension may increase by many orders of magnitude with the addition of a small number of particles. Historically these systems have been modeled either by tracking individual particles (which rapidly becomes prohibitively computationally expensive as the number of particles increases), or by taking a phenomenological continuum approach in which the nonlinearities are measured experimentally for specific systems rather than derived from microscopic principles.
In this project we have developed a hybrid approach which operates at the mesoscale and hence reduces computational cost (relative to MD approaches) while maintaining a direct link between effective material properties and microscopic dynamics.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received		Paper
08/21/2013	1.00	Pawel J. Zimoch, Gareth H. McKinley, A. E. Hosoi. Capillary Breakup of Discontinuously Rate Thickening Suspensions, Physical Review Letters, (07 2013): 36001. doi: 10.1103/PhysRevLett.111.036001
TOTAL:	**1**	

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received	Paper
TOTAL:	

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

APS Fellow (Hosoi, 2012)
I. E. Block Community Lecturer (SIAM Award) (Hosoi, 2013)

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Pawel Zimoch	1.00	
FTE Equivalent:	**1.00**	
Total Number:	**1**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Anette Hosoi	0.04	
FTE Equivalent:	**0.04**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

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Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME
Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See attachement.

Technology Transfer

FINAL REPORT: DEVELOPING NOVEL FRAMEWORKS FOR MANY-BODY ENSEMBLES

MIT Technical PoC: A. E. Hosoi (peko@mit.edu)
ARO Technical PoC: Samuel Stanton, (Samuel.c.stanton@us.army.mil)
Date: March 17, 2016

Summary. In this project we have made strides towards developing a mesoscopic statistical framework (MSF) to model non-equilibrium ensembles comprised of large numbers of simple components. As a testbed, we have considered inhomogeneity formation in driven non-equilibrium systems, namely we seek to predict whether inhomogeneities appear and to develop a description of inhomogeneity formation that is valid across particle and system scales. These systems can be tricky to analyze as mesoscale structures can lead to highly nonlinear macroscopic responses e.g. near a critical concentration, the effective yield stress and viscosity of a suspension may increase by many orders of magnitude with the addition of a small number of particles. Historically these systems have been modeled either by tracking individual particles (which rapidly becomes prohibitively computationally expensive as the number of particles increases), or by taking a phenomenological continuum approach in which the nonlinearities are measured experimentally for specific systems rather than derived from microscopic principles.

In this project we have developed a hybrid approach which operates at the mesoscale and hence reduces computational cost (relative to MD approaches) while maintaining a direct link between effective material properties and microscopic dynamics. We are particularly interested in systems in which the microscopic dynamics of the system are known and reversible (e.g. suspensions of particles in Stokes flow). These assumptions allow us to take advantage of Markovian approaches hence the primary challenges of the project centered on developing coarse-grained statistical descriptions of states that are valid at different length scales, and qualifying transition probabilities between states.

Figure 1 presents a graphical overview of our method which required the development of novel approaches to: (1) identify clusters and states, (2) quantify transition probabilities, and (3) map these states and transitions onto a Markovian model. To focus our efforts, we chose to study the process of cluster development in systems composed of multiple particles interacting in simple ways (e.g. dense particulate suspensions). In particular we have applied our approach to three model systems:

1. *One -dimensional "blocks in a box."* Blocks, initially randomly placed on the grid, undergo random motion due to the grid's coupling to a thermal reservoir.

2. *Driven spherical particles without hydrodynamic interactions.* The particles are divided into two species distinguished by the direction of the forcing. Particles do not experience hydrodynamic forces due to the motion of other particles, but do undergo thermal Brownian motion. The particles interact with one another solely through hard-core repulsive

		1D Toy model	2D/3D without hydrodynamics	2D/3D with hydrodynamics
MSF	Description	●●●	●●●	●●●
	Transitions	●●○	●○○	○○○
	Markov chain	●●●	●●●	●●●
	Why do clusters form?	●●●	●○○	●○○
	How do clusters form?	●●○	●○○	○○○

Table 1: Progress to date. ●●● = completed, ●●○ = substantial progress, ●○○ = preliminary results. MSF = mesoscopic statistical framework. Note that our focus has been on developing the MSF (white region of the table) and we are currently finalizing measurements of transition probabilities in all three systems. Grey regions indicate promising new directions and questions to address using our new hybrid approach.

interactions.

3. *Spherical particles with hydrodynamic interactions.* Particles are neutrally buoyant, suspended in a Newtonian fluid and driven by an externally imposed shear flow.

In all three systems our goal is to apply our novel coarse-grained approach to predict the conditions under which clustering occurs. This perspective can also be used to shed light on questions related to why clusters form, what features of the microscopic dynamics drive clustering, and quantification of growth and evolution of cluster size at different length scales as the system evolves. While we have made significant advances along these lines, our results have also opened up a number of new promising avenues of investigation. Progress of the project to date is summarized in Table 1.

Key advances:

- Adopting a dendrogram approach to describe large particle ensembles. This was an important insight that enabled us to rigorously distinguish clustered and non-clustered states.
- State identification based on dendrogram properties which provides a novel means of coarse graining via statistical properties of the ensemble.
- Quantification of transition probabilities between states in three canonical systems of increasing physical complexity.
- Integration of the three advances above into a Markovian model (in progress).

Products:

- Zimoch, McKinley, and Hosoi. "Capillary Breakup of Discontinuously Rate Thickening Suspensions." *PRL* **111**, 036001 (2013).
- Zimoch and Hosoi. "Cluster identification in particle suspensions." (In progress).
- Zimoch and Hosoi. "Hybrid statistical approaches to predict clustering in many-body systems." (In progress).

Personnel: Pawel Zimoch (graduate student, MIT), A. E. Hosoi (PI, MIT).

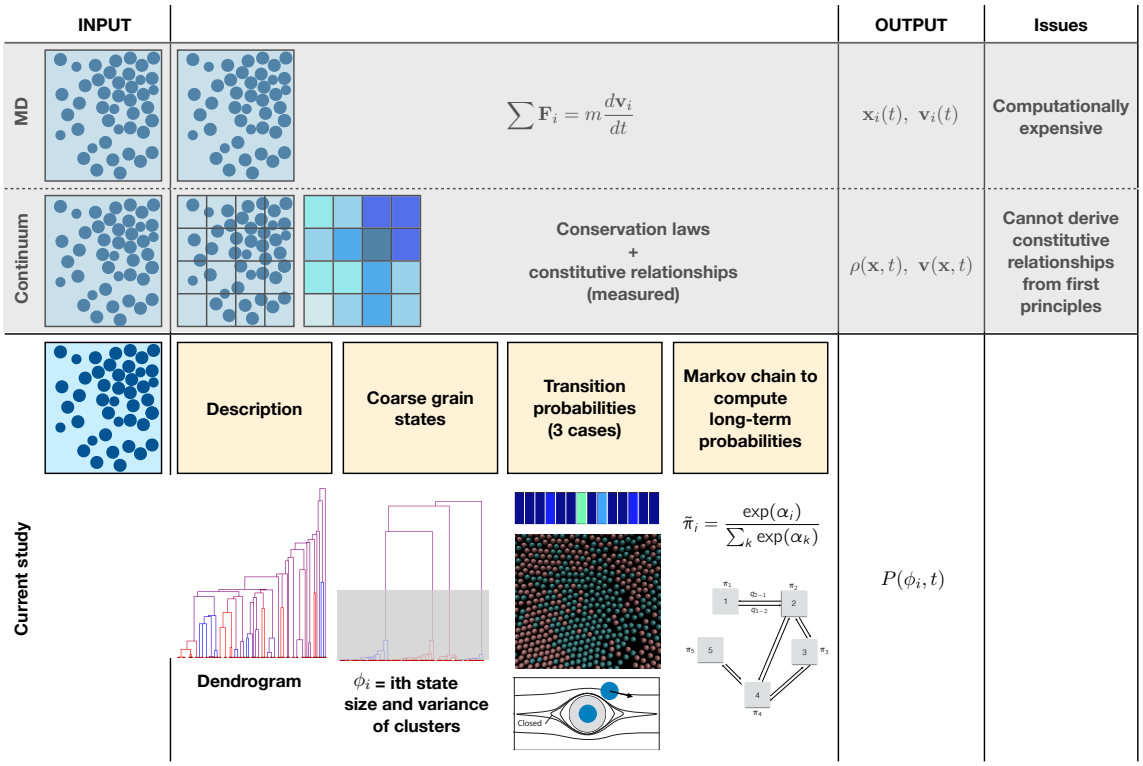

Figure 1: Graphical overview of our mesoscale approach. Coarse-grained description, state identification, and Markov chain analysis are all generalizable to a wide array of systems. Transition probabilities are unique to each specific case and reflect the physical dynamics relevant for particular systems.

A. Background. The fundamental assumption of equilibrium thermodynamics dictates that all microstates of an isolated system can be observed with equal probability. In the majority of systems made up of simple particles, this assumption leads to a homogeneous distribution of particles and orientations. Notable exceptions are systems in which topological constraints make more phase space available to non-homogeneous configurations, e.g. cubes in a confined space, or elongated rods. In this project, however, we focus on systems made up of simple spheres in which homogeneous behavior is extremely common. And yet, even for these simple cases, when the system is driven away from equilibrium by an externally applied force, mass may no longer be homogeneously distributed and clumps or "clusters" may appear. Such systems are challenging to analyze because they do not obey the symmetries utilized in the analysis of equilibrium systems or systems that can be treated as a continuum.

Historically these types of systems have been modeled using two types of strategies (see first and second row in Figure 1). At the particle scale (top row), two commonly made assumptions are that particles either do not interact with each other, or that for each particle this interaction can be averaged over all other particles, as if each particle was placed in a "mean-field." In non-equilibrium systems such as particulate suspensions, where multi-particle interactions can play a key role in the nonlinear macroscopic response of the system, the complexity of particle-particle interactions quickly renders analysis intractable. In the current state-of-the-art, we have a good understanding of two-particle interactions. Although the effect of interactions between sets of three particles has been investigated (see e.g. work by Jeff Morris), no general framework exists.

At the other end of the spectrum at the system scale (second row in in Figure 1), equilibrium or near-equilibrium systems can be approximated as continua, and long-wavelength (hydrodynamic) descriptions can be obtained by averaging on a scale larger than individual particles but smaller than the characteristic scale associated with variations of macroscopic properties. In non-equilibrium systems, such as polymer melts and other complex fluids, there are few first-principles derivations of macroscopic material behavior. Instead, material properties are extracted by fitting parameter values in phenomenological models to experimental data.

Bringing these microscopic and macroscopic worlds together presents a significant challenge. What happens at the intermediate mesoscales? In equilibrium statistical mechanics, this question is answered by the theory of renormalization, which shows how interactions between different components of a system change as the descriptive length scale changes. No equivalent theory exists in the non-equilibrium world. This is problematic as the process of inhomogeneity development occurs primarily at the mesoscale. Therefore, there is a need for a framework that captures the structure of non-equilibrium systems as they evolve at scales larger than a single particle, but smaller than the entire system. This research project aims to address this gap in our understanding.

B. Identifying and coarse-graining states. There are four essential components to our approach: 1) state identification, 2) coarse-graining, 3) estimating transition probabilities and 4) adapting Markovian approaches to capture out-of-equilibrium dynamics and to estimate prob-

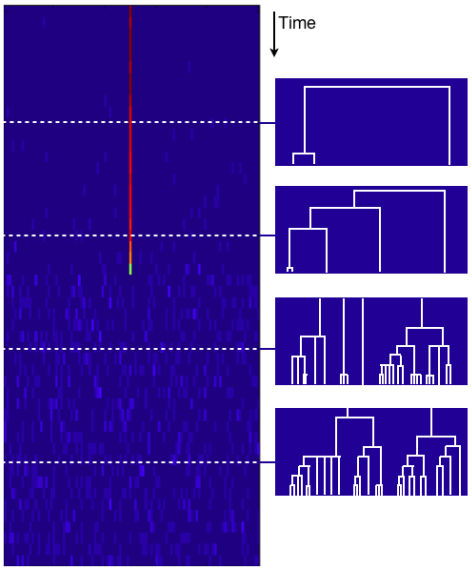

Figure 2: Illustration of the dendrogram representation. The rectangle on the left shows the evolution of blocks on a grid, at $T = 4$, from an initial condition where all blocks are stacked at the center of the grid. Color indicates the number of blocks are each grid point, with red indicating high, and blue indicating low. This simulation was carried out with 30 blocks on a grid with 100 locations. After approximately $25,000$ time steps, the large center cluster falls apart due to the relatively high temperature. Dendrograms represent four snapshots at different times as indicated by the dash white lines.

abilities of observing equilibrium configurations. The two historical approaches – molecular dynamics and continuum approaches – produce outputs that are tied to a global reference frame such as particle position $\mathbf{x}(t)$ or spatially varying densities $\rho(\mathbf{x}, t)$. In contrast, our approach takes a state-centric view in which we compute the probability of observing a state S_i independent of global position or orientation (e.g. in a non homogeneous state, we typically do not need to know the positions of each of the individual clusters, rather we are interested in the characteristic size and distribution of clusters).

To achieve this, we borrow a strategy from computational biology that captures the hierarchical nature of clustering, namely the dendrogram (see Figure 2). Connections in the dendrogram represent particles that are "close" as defined by a distance metric which typically combines instantaneous relative velocity and position. States are defined by the structure of the dendrogram. In addition the to the appealing state-centric nature of this type of representation, dendrograms also provide an intuitive means of blending the discrete nature of the particles (typically Lagrangian) with the continuum nature of the surrounding fluid (typically Eulerian). Finally the dendrograms naturally lend themselves to coarse-graining which can be accomplished by selecting a characteristic scale and selecting a low dimensional representation of detailed structure below this cut-off (e.g. characteristic mean and variance of the number of particles in each cluster).

C. Transition probabilities: three model systems. The dendrogram coarse-graining approach and Markovian dynamics can be universally applied to a wide variety of systems, however the physical details that are unique to each individual systems must be captured in the transition probabilities between states. Ultimately we would like to be able to derive these transition probabilities from microscopic dynamics however, to demonstrate the effectiveness of our ap-

proach, we begin by measuring these transition probabilities in reduced scale simulations, three of which are described below.

Toy model: Blocks in a box. The simplest system we use to test our framework is a one-dimensional discrete system with well-defined transition probabilities between microstates. Consider a 1D domain with a periodic array of N discrete spaces coupled to a thermal bath at temperature T. In these spaces, there reside n blocks of unit mass. There is no limit to the number of blocks that can reside in a single space; blocks that occupy the same space are stacked on top of one another. There are no energetic interactions between the blocks. For a block to pass another block, the two must first form an intermediate state that consists of a tower of height $h = 2$ blocks. In the absence of block interactions, each configuration has the same energy, so the blocks undergo a diffusive random motion on the periodic array. As a result, each configuration of the blocks is equally likely. However, when a "gravitational field" is present – namely an external potential that varies with the vertical position of the block – a block can change its energy via stacking. While stacking decreases the energy of the system, there are fewer stacked configurations than unstacked configurations, so entropy drives the system towards disorder. Thus, the blocks evolve under two competing effects: the energy drives the system towards stacked blocks, i.e. vertical clustering, and the system's entropy drives it towards disaggregation. The relative magnitude of these two effects – and hence the equilibrium distribution – depends on the temperature of the thermal bath to which the system is coupled.

The dynamics of the simulation can take several different forms, and the detailed statistics of cluster formation depend on the specific form of the chosen transition probabilities. As a concrete example, consider Gibbs sampling. In this case, the system evolves in discrete time steps. At each step, one particle is chosen at random, and a move to the left or to the right is proposed with equal probability. The energy of a configuration is calculated as

$$E_{proposed} = \sum_{i}^{n} h_i \times G \tag{1}$$

where G is the strength of the gravitational field and h_i is the location above the base level of the i^{th} block. The proposed motion is then accepted with probability

$$P = \frac{\exp(E_{proposed}/T)}{\exp(E_{proposed}/T) + \exp(E_{current}/T)}. \tag{2}$$

Since there are no energetic interactions between particles themselves, the strength of the gravitational field G can be set to 1, without loss of generality. The behavior of the system is then controlled solely by the temperature of the bath, T which can be tuned to shift the equilibrium distribution from a clustered to an unclustered state.

Driven particles without hydrodynamic interactions. The second model consists of spherical particles enclosed in a two-dimensional box with periodic boundaries. Particles interact with each other thorough hard-core dissipative interactions which are critical to the entropic nature of

the force driving the clustering. There are no hydrodynamic interactions between particles, but each particle individually behaves as if it was immersed in a fluid at a finite temperature hence the particles undergo Brownian motion. After the system reaches equilibrium at a prescribed temperature, a force is applied to each particle. The particles are divided into two species driven with forces of equal magnitude but in opposite directions. This results in frequent collisions between particles traveling in opposite direction, but less frequent collisions between particles of the same species. As a result, the particles separate into "lanes", each containing a single particle species.

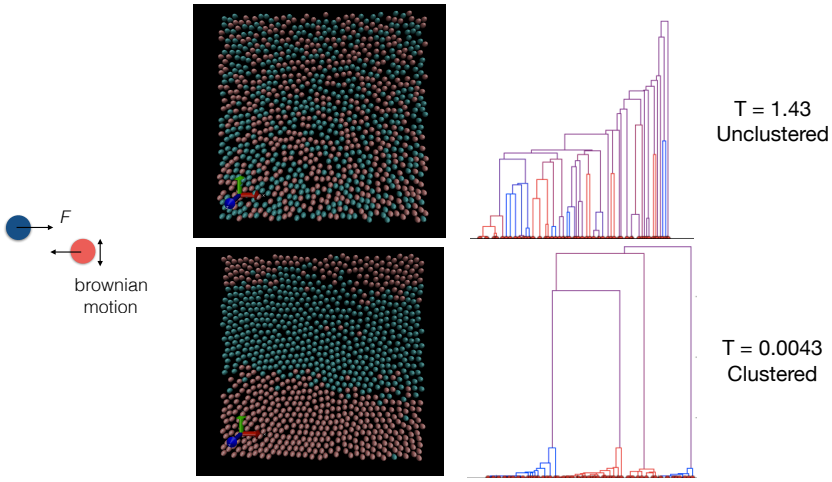

Figure 3: (A) The forced particle model consists of two species of particles, forced in opposite directions. The particles experience a viscous drag and stochastic brownian forces due to the surrounding fluid bath, but no hydrodynamic interaction forces. (b-d) Typical frames from the simulation, in progressive stages of segregation of particles. (b) Particles just before the forcing is applied. (c) Particles begin to segregation. (d) Long term steady-state of the system, with particles segregated into two streams.

The simulations are carried out using the HOOMD-Blue molecular dynamics package, developed by the Glotzer lab at the University of Michigan. The forcing scheme and a typical simulation result along with the concomitant dendrograms is shown in figure 3.

Particles in a shear field, with hydrodynamic interactions. The third model is composed of spherical particles enclosed in a two-dimensional box with periodic boundary conditions. The particles are embedded in a viscous fluid and interact with each other through low Reynolds number hydrodynamic forces. Therefore, the motion of any particle results in a net hydrodynamic force exerted on the other particles. These interactions are purely dissipative and long range ($\sim 1/r$). Energy is input via a steady shearing flow field.

The simulations on this model are performed using a Stokesian Dynamics code developed by

James Brady at Caltech and Jim Swan at MIT (formerly Caltech). To discern the essential nature of particle pair interactions, we begin by considering an ensemble of particle-pair collisions in isolation as illustrated in Figure 4. Starting from random initial conditions, an ensemble of particle pairs was simulated to establish the long-time particle pair probability density distribution, which shows the probability of observing a particle pair in a given configuration. Particles are far more likely to be observed close to each other (indicated by the bright band in Figure 4, bottom right) because the relative motion of the particles in these configurations is slow. In contrast, the relative motion of particles when they are far from each other is fast, resulting in low overall probability of observing particles in such configurations. Note that this clustering occurs even though there are no attractive forces between the particles; rather the time-averaged dynamics are such that the particles are far more likely to be observed close to each other than far away.

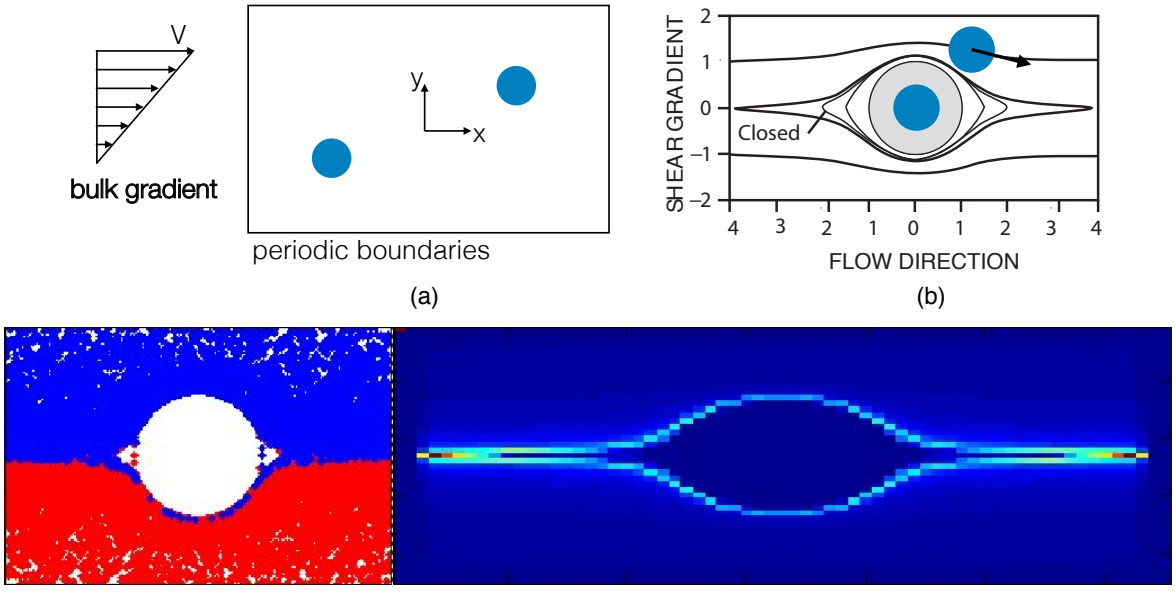

Figure 4: (a) A pair of particles in a periodic bounding box, subjected to uniform shear. (b) Schematic of trajectories of the particle pair in steady uniform shear, in the frame of reference centered on one of the particles. It is a well-known phenomenon that some trajectories are "closed", meaning that the particles never separate from each other. (Bottom) Snapshots of a pair collision ensemble simulation. (Left) One of the particles is located at the center of the image (not shown), while the other particle is represented by a single point, blue or red. Each point represents one simulation. Blue and red points are reflections of each other about the center of the image. The white region at the center of the image shows the excluded volume due to the presence of a particle at the center of the image. (Right) Time-averaged locations of the particle pair. Bright colors indicate regions where the second particle is more likely to be observed.

D. Markovian model. Having identified the coarse-grained system states S_n and transition

probabilities $q_{i\to j}$ between states, it is a straightforward exercise to apply a Markovian analysis to evolve the system though non-equilibrium configurations and compute probabilities of observing equilibrium states by invoking principles of detailed balance. Consider a trajectory through state space denoted by:

$$\mathbf{S} = (S = m, S_1, S_2, ...S_N, S = n).$$

Given transition probabilities $q_{i\to j}$ which are dictated by the dynamics, we seek the evolution of the probability of observing state i at time t, $\pi_i(t)$, and the long-term probability of observing state i, $\overline{\pi_i}$. The first can be computed by iteratively applying the transition probability matrix to the initial state. The second can be directly computed as

$$\overline{\pi_i} = \frac{e^{\alpha_i}}{\sum_k e^{\alpha_k}}$$

where

$$\alpha_n = \log\left(\frac{\pi_n}{\pi_m}\right) = \log\left(\frac{q_{m\to S_1}}{q_{S_1\to m}}\right) + \sum_{i=1}^{N} \log\left(\frac{q_{S_i\to S_{i+1}}}{q_{S_{i+1}\to S_i}}\right) + \log\left(\frac{q_{N\to n}}{q_{n\to N}}\right).$$

The final stage of this project is the integration of all of the components described above. In each of the three systems (blocks in a box, particles without hydrodynamics, and particles with hydrodynamics) we can represent states of the system by dendrograms (examples shown in Figures 2 and 3). These dendrograms are then coarse-grained and classified. Finally transition probabilities between these classifications can be measured numerically (currently underway) and predictions from the Markov model can be compared with full MD simulations.